Complexation of Gadolinium Ion with Poly(methacrylic acid)s and Magnetic Properties of the Complexes

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Abstract

The complexation of gadolinium (Gd^{3+}) ion with poly(methacrylic acid) and its copolymers was studied. Poly(methacrylic acid-co-acrylamide) formed the tris(carboxylate)-coordinate gadolinium complex with an extra large complex formation constant, while poly(methacrylic acid) formed the bis-coordinate complex. Transparent and flexible film containing a high proportion of Gd ion was prepared by casting the complex solution of poly(methacrylic acid-co-methylacrylate). The complexed Gd ion was uniformly dispersed in the film and showed paramagnetism. The formation and magnetic properties of the polymer–Gd complexes are discussed in comparison with those of the corresponding iron complexes.

Introduction

Rare earth elements show characteristic physicochemical properties due to their 4f electrons, and polymer composites containing these rare earth elements have been often studied and utilized as fluorescent, laser and magnetic materials. There is much interest in the synthesis of a polymer–metal complex in an attempt to find an organic polymer with inorganic functions [1]. However, the polymer complexes with rare earth ions where the ions are coordinately bound to polymer chains have not been studied, except for Okamoto *et al.* who recently reported the preparation of polymer europium and terbium complexes and their fluorescent properties [2–4]. Most rare earth ions have 1–7 unpaired electrons on their inner 4f orbitals and they have large magnetic moments. But magnetic properties of the polymers complexed with rare earth ions have not been reported. In this paper, the complexation and magnetic properties of gadolinium(III) (Gd^{3+}) ion with poly(methacrylic acid) and its copolymers were studied in comparison with those of iron(III) ions.

Experimental

Materials and Methods

Poly(methacrylic acid) (PMA), poly(methacrylic acid-co-methylacrylate) (MMA), poly(methacrylic acid-co-ethylacrylate) (MEA), and poly(methacrylic acid-co-acrylamide) (MAA) were prepared by radical polymerization. Compositions and molecular weights of the polymers were determined by elemental analysis and gel permeation chromatography (polystyrene standard), respectively. In the following, the suffix indicates the mole fraction of the methacrylic acid residue in the copolymer. Molecular weight of PMA = 3.0×10^5, $MMA_{0.73} = 2.0 \times 10^5$, $MMA_{0.48} = 1.6 \times 10^5$, $MMA_{0.35} = 1.6 \times 10^5$, $MMA_{0.25} = 1.6 \times 10^5$, $MEA_{0.25} = 1.8 \times 10^5$, $MEA_{0.20} = 1.6 \times 10^5$, $MEA_{0.16} = 2.0 \times 10^5$ and $MAA_{0.28} = 2.0 \times 10^5$. Analytical grade reagents of gadolinium nitrate and iron nitrate were used.

Polymer Complex Films

Methanol solutions of the copolymer and the gadolinium salt were mixed and stirred for several hours. The complex solution was cast on a Teflon plate and dried under saturated methanol vapor for 2 days, under air atmosphere for one day, and *in vacuo* at 50 °C for 2 days. Corresponding iron complex films were prepared by the same procedure.

Viscometric Measurements

The viscosity of the polymer solution was measured with an Ubbelohde viscometer at 30 °C.

Potentiometric Titrations

All titrations were carried out under nitrogen atmosphere using CO_2-free water. Hydrogen ion activities were determined with a glass electrode and a TOA HM-15A type pH meter. Sodium nitrate was added as supporting electrolyte (0.1 M).

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Spectral Measurements

IR spectra of the films were measured with a JASCO IRA-1. X-ray diffraction and X-ray microanalyses were measured with a Rigakudenki model 2026 and a JEOL JXA-733, respectively.

Magnetic Measurements

Magnetic susceptibility was measured with a Faraday-type magnetic lever using Gd_2O_3 as standard (22 ℃; $1.38_2 \times 10^{-4}$ emu g^{-1}).

Results and Discussion

By adding gadolinium salt to the methanolic solution of PMA, MMA and MEA, the polymer–Gd complex was formed. Viscosity of the MMA solution in the presence of Gd was measured to study this complexation (Fig. 1). At constant concentration of the polymer, an increase in the amount of Gd ion added causes a decrease in the viscosity, revealing that the polymer chain is contracted due to intrapolymer chelation. In Fig. 1, the viscosity of polymer solution in the presence of Fe^{3+} or Al^{3+} ion is also given. The polymer chain is more contracted with Al than with Gd. On the other hand, the viscosity increases slightly with Fe, which suggests an interpolymer chelation. This result means that Gd ion forms an intrapolymer-type complex with MMA and that the polymer chain complexed with Gd is not much contracted through chelation and gives a flexible film after the removal of solvent.

Potentiometric titration was carried out for the aqueous solution of Gd ion with PMA and MAA. MAA is a water-soluble model polymer of MMA and MEA. The PMA and MAA complexes with Gd ion behave as polyelectrolytes in aqueous solution, so that the modified Bjerrum method reported by Gregor [5] was used for calculation of the following equilibrium constants b_n and formation constants k_n. Acid dissociation constants K_a were estimated from Henderson–Hasselbach plots (for the Fe complexes the modified Bjerrum method could not be applied because of hydrolysis of the Fe ion during the titration).

$$RCOOH + Gd^{3+} \overset{b_1}{\rightleftharpoons} (RCOO)Gd^{2+} + H^+ \tag{1}$$

$$RCOOH + (RCOO)Gd^{2+} \overset{b_2}{\rightleftharpoons} (RCOO)_2Gd^+ + H^+ \tag{2}$$

$$RCOOH + (RCOO)_2Gd^+ \overset{b_3}{\rightleftharpoons} (RCOO)_3Gd + H^+ \tag{3}$$

$$RCOO^- + Gd^{3+} \overset{k_1}{\rightleftharpoons} (RCOO)Gd^{2+} \tag{4}$$

$$RCOO^- + (RCOO)Gd^{2+} \overset{k_2}{\rightleftharpoons} (RCOO)_2Gd^+ \tag{5}$$

$$RCOO^- + (RCOO)_2Gd^+ \overset{k_3}{\rightleftharpoons} (RCOO)_3Gd \tag{6}$$

The calculated formation curves for PMA, $MAA_{0.28}$ and methacrylic acid monomer (MA) are shown in Fig. 2, where $\bar{n}$ is the average number of complexed carboxylate groups per Gd ion and [LH] is the concentration of carboxylic acid. The formation curves of $MAA_{0.28}$ and MA–Gd appear to extrapolate to a maximum coordination number of 3, indicating that the complexation is completed at Gd(carboxylate)$_3$. On the other hand, the formation curve of PMA–Gd extrapolates to a maximun coordination number of 2, indicating the complexation is retained at the formation of Gd(carboxylate)$_2^+$.

Successive formation constants k_i

$$k_i = b_i/K_a \tag{7}$$

and overall formation constants

$$\beta_n = \prod_{i=1}^{n} k_i \tag{8}$$

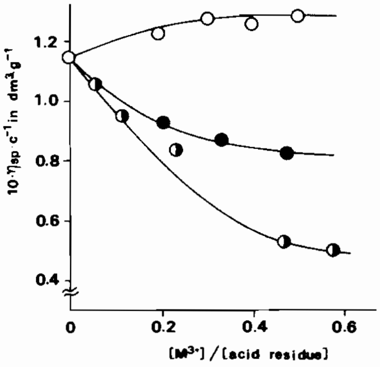

Fig. 1. Reduced viscosity of the methanolic solution of $MMA_{0.35}$ in the presence of Gd (●), Fe (○), and Al (◑) ion [carboxylic acid residue of MMA] = 1 mmol dm^{-3}, 30 °C.

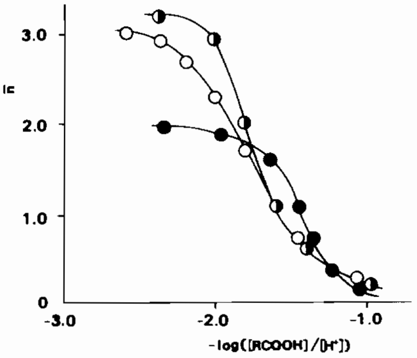

Fig. 2. Bjerrum's formation curves for the Gd complex with PMA (●), $MAA_{0.28}$ (○), and MA (◑). $[NaNO_3]$ = 0.1 mol dm^{-3}, 30 °C.

TABLE I. Complexation Constants of the Gd Complexes

Carboxylic acid	$\bar{n}$	$\log b_1$	$\log b_2$	$\log b_3$	$\log B_n$	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_n$
$MAA_{0.28}$	3.0	−1.6	−2.1	−2.4	−6.1	4.3	3.8	3.5	11.6
PMA	2.0	−1.5	−1.8		−3.3	4.6	4.3		8.9
MA	3.2	−1.3	−1.8	−2.0	−5.1	3.2	3.2	2.7	8.4

for the complexation of Gd ion with carboxylic acids are summarized in Table I. Values of k_1 and k_2 for the Gd complex with PMA were *ca.* 10 times larger than those with low molecular MA. However, the third step of the carboxylate-complexation was not observed and β_n was limited to *ca.* 10^9. It is assumed that the PMA chain cannot easily form the tris-coordinate complex with its three carboxylate groups due to steric hindrance of the polymer chain and apparently 'large' Gd ion. On the other hand, the Gd ion complexation proceeded to the third step for MAA; β_n was *ca.* 10^3 times larger than those of PMA and MA, and the MAA formed a very stable tris-coordinate complex with Gd ion. It is considered that the comonomer residue on MAA decreases the steric hindrance for the complexation.

Polymer complex films were prepared by casting the complex solutions containing various amounts of Gd ion for PMA, MMA and MEA. Only $MMA_{0.35}$ gave flexible and transparent complex films independent of the Gd ion content. PMA, $MMA_{0.73}$ and $MMA_{0.48}$ gave clear but less flexible films, and $MMA_{0.25}$ gave a less clear one when the Gd content was increased. MEA gave flexible and transparent films but they degraded after a few days. Of the Fe complexes, $MMA_{0.35}$ for example gave a clear red film at low Fe ion content and a cloudy brown one at the higher content, but the films were not flexible, which corresponded to the viscometric measurement mentioned above.

IR spectra of the complex films were measured to estimate the complexation in the films. While $\nu_{C=O}(-COOH)$ of $MMA_{0.35}$ appears at 1700 cm^{-1} and $\nu_{C=O}(-COO^-)$ of the $MMA_{0.35}$–Na salt appears at 1630 cm^{-1}, $\nu_{C=O}(-COO^-)$ of the $MMA_{0.35}$–Gd complex shifts to lower wave number (1620 cm^{-1}). The $MMA_{0.35}$–Fe complex film showed the same spectra. This shift suggests complexation between carboxylate and Gd or Fe ion.

X-ray diffraction patterns of the $MMA_{0.35}$–Gd complex film are shown in Fig. 3. In the case of $MMA_{0.35}$, a hollow peak due to stereoregularity of the polymer is observed (a). This peak disappears as the Gd or Fe ion content increases (b, c or e, f), and the sharp peaks of gadolinium nitrate (d) or iron nitrate (g) are also not observed. This suggests that the metal ion is dispersed uniformly in the film. X-ray microanalysis also supports a uniform dispersion of the metal ion in the films.

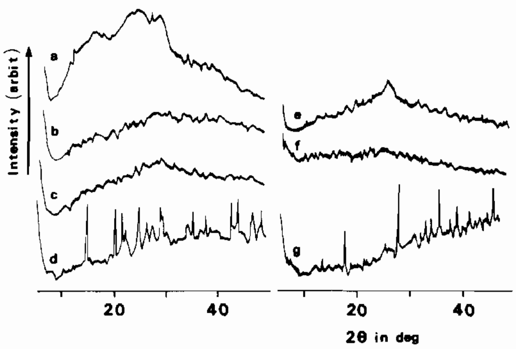

Fig. 3. X-ray diffraction patterns of the $MMA_{0.35}$–Gd and –Fe complex films. (a) $MMA_{0.35}$; $MMA_{0.35}$–Gd or –Fe (b, e) [Gd or Fe]/[acid residue] = 1/50, (c, f) [Gd or Fe]/[acid residue] = 1/3; (d) $Gd(NO_3)_3$ salt; (g) $Fe(NO_3)_3$ salt.

Magnetic susceptibility of the complex films was estimated by the Faraday method. After diamagnetic correction, molar magnetic susceptibilities and effective Bohr magneton of Gd and Fe ions in the films were calculated and are summarized in Table II. Gd ion in the films shows constant molar magnetic susceptibility and effective Bohr magneton regardless of its content (2.7×10^{-2} emu mol^{-1}, 8.0 B.M. at room temperature, 1.0×10^{-1} emu mol^{-1} at liquid nitrogen temperature). These values correspond to theoretical ones derived from Curie's law. This result indicates that Gd ion in the films is paramagnetic. On the other hand, the effective Bohr magneton of Fe ion in the films depends on temperature and Fe content, which means an antiferromagnetic interaction among the Fe ions or formation of a low spin Fe complex. Fe ion has 5 unpaired electrons in its outer 3d orbital, so it is easily affected by the structure of the complex and/or neighbouring iron ions. On the other hand, Gd ion has 7 unpaired electrons on the inner 4f orbital which is shielded enough and Gd ion shows its magnetic property even in the polymer film.

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TABLE II. Magnetic susceptibility of Gd and Fe ions in the complex films

Sample	Gd^{3+} or Fe^{3+} content (wt.%)	Magnetic susceptibility				Effective Bohr magneton μ_{eff}(B.M.)	
		at 295 K		at 77 K			
		$\chi_{ob} \times 10^5$ (emu/g)	$\chi_{Gd} \times 10^2$ (emu/mol)	$\chi_{ob} \times 10^5$ (emu/g)	$\chi_{Gd} \times 10^1$ (emu/mol)	at 295 K	at 77 K
$MMA_{0.35}$–Gd	5.68	0.9(8)	2.8(7)	3.4(7)	0.9(8)	8.2	7.8
	13.4	2.2(3)	2.6(8)	8.4(5)	0.9(9)	8.0	7.9
	14.6	2.4(3)	2.6(6)	9.4(9)	1.0(1)	8.0	7.9
$Gd(NO_3)_3$	34.8	5.9(1)	2.6(8)	23.4(0)	1.0(6)	8.0	8.0
theoretical			2.7(1)		1.0(4)	8.0	8.0
$MMA_{0.35}$–Fe	2.57	0.2(8)	0.7(2)	0.5(1)	0.1(2)	4.1	2.7
	5.43	0.8(2)	0.8(9)	0.1(5)	0.1(6)	4.6	3.1
$Fe(NO_3)_3$	13.8		1.5(2)			5.9	
theoretical			1.4(7)		0.5(6)	5.9	5.9

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